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# Timescales of magmatic processes at Ruapehu volcano from diffusion chronometry and their comparison to monitoring data

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## Abstract

Recent eruptions from Mt. Ruapehu have been difficult to predict, despite the presence of a multi-parametric monitoring network. As a result, it is necessary to assess precursory signals prior to an eruption and align those to magmatic processes at depth. Fortunately, scoria from all historical Ruapehu eruptions contains pyroxene crystals that are strongly reversely zoned in the form of a thin (2 to 3  $\mu\text{m}$ ), outermost rim. These crystals therefore preserved changes in the magmatic system soon before their eruption. We used experimentally determined diffusion coefficients to assess the timescales of magma-magma interaction, and compared those to the monitoring record. Four of the five eruptions analysed (1969, 1971, 1977, 1995) gave diffusion timescales  $\sim 3$  to 5 months before their eruption, with an increased number of crystals recording timescales within 1 month of eruption. Pyroxene crystals from the 1996 eruption record events that occurred prior to and during the 1995 eruption suggesting that the bulk of the 1996 crystals were derived from the 1995 magma. These diffusion timescales do not compare well to a change in any monitoring signal before historical eruptions. However, an examination of recent seismicity (2005-2013) since a significant upgrade (both in number of stations and type of seismometers) showed that two phreatic eruptions in 2006 and 2007 were preceded by a seismic swarm from  $\sim 5$  to 15 km depth,  $\sim 3$  to 5 months before each eruption - consistent with the diffusion timescales. Based on this correlation, deep seismic swarms likely indicate a period of pressurisation in the magmatic system, which may lead to gas-rich, phreatic eruptions.

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## 1. Research highlights

- Diffusion chronometry has been completed on pyroxenes (clinopyroxene and orthopyroxene) from five historical eruptions at Mt. Ruapehu
- All diffusion timescales record a period of magma injection 3-5 months before each eruption
- There is good agreement between deep seismicity and diffusion chronometry
- Two phreatic eruptions occurred  $\sim 5$  months after deep seismic swarms, which may suggest that such swarms are a good medium-term eruption precursor

## 2. Introduction

Volcanic eruptions are often preceded by the influx of fresh, hot magma into a pre-existing magma reservoir (e.g., Murphy et al., 1998; Leonard et al., 2002) accompanied by convective overturn and mixing or by self-mixing (Couch et al., 2001; Burgisser and Bergantz, 2011). These interactions may occur shortly before an eruption, but in many cases, their exact pre-eruptive timing is unknown. Clearly, an understanding of the timescales of magma/crystal interaction prior to previous eruptions from a particular volcano would be extremely useful in forecasting an impending eruption and/or interpreting monitoring signals. In order to determine these timescales, a number of researchers have examined the compositional history preserved in magmatic crystals. For instance, some workers determined magma residence times using Sr diffusion in plagioclase (Zellmer et al., 1999), and Fe-Mg diffusion in both olivine (Gerlach and Grove, 1982) and clinopyroxene (Morgan et al., 2004). In addition, the zoning patterns and diffusion profiles of many crystals within a single eruption can be used to constrain the time taken to assemble and erupt a magma reservoir (Morgan et al., 2004; Druitt et al., 2012), determine the time between recharge and eruption (Zellmer et al., 2003; Martin et al., 2008; Druitt et al., 2012; Saunders et al., 2012a; Charlier et al., 2012), and track the fate of crystals transported between distinct magmatic storage regions (Kahl et al., 2011, 2013). All of these studies can be used to help constrain the timing of magma mixing and eruption.

Previous diffusion studies have been conducted on olivine, clinopyroxene, orthopyroxene, quartz and plagioclase crystals, testifying to the broad applicability of diffusion chronometry for a wide range of conditions and volcanic settings. In some cases, the calculated timescales correspond well to deep seismicity and SO<sub>2</sub> flux (Saunders et al., 2012a) and assumed deformation (Druitt et al., 2012; Kahl et al., 2011, 2013; Costa et al., 2013), months to decades before eruption.

Eruptions at Ruapehu volcano, New Zealand, have often occurred without adequate warning (Nairn et al., 1979; Christenson et al., 2010; Jolly et al., 2010; Kilgour et al., 2010), which is significant given the numbers of recreational users (hiking and skiing) on the mountain during the summer and winter months. Historical eruptions at Ruapehu have also been driven by very small-volume ( $< 0.01 \text{ km}^3$ ) magmas within a very complex, open magmatic system (Gamble et al., 1999; Kilgour et al., 2013). Magmas ascending beneath Ruapehu likely interact with remnant magmas and crystal mush zones (Nakagawa et al., 1999, 2002; Kilgour et al., 2013), leading to chemical interactions between new magma and resident crystals. Ruapehu scoria contain pyroxene macrocrysts ( $> 100 \text{ }\mu\text{m}$ ) and microlites ( $< 100 \text{ }\mu\text{m}$ ) that are clearly zoned in Fe and Mg (Nakagawa et al., 2002). With time the interface between the overgrowth rims and crystal cores become modified by Fe-Mg diffusion. Therefore, crystals from historical eruptions at Ruapehu are suitable for examining the timescales of magmatic interactions prior to eruption.

Monitoring of Ruapehu activity has involved regular Crater Lake sampling for fluid chemistry along with measured temperature, in conjunction with a developing seismic and GPS network since the mid-1960's. The aim of this work is to combine the record preserved in zoned pyroxene crystals with the long-term monitoring dataset to evaluate temporal links between the addition of new magma to the plumbing system and the monitoring signals, in particular those associated with the most common type of eruption at Ruapehu - phreatic eruptions, which are thought to be driven by magmatic gases (Christenson et al., 2010).

### 3. Geological background

Ruapehu is a frequently active, andesitic cone volcano located at the southern end of the Taupo Volcanic Zone (TVZ) (Fig. 1). Active since  $\sim 250,000 \text{ yr}$  (Tanaka et al., 1997; Gamble et al., 2003), Ruapehu has been constructed by at least four main lava flow formations (Hackett, 1985; Hackett and Houghton, 1989; Price et al., 2012). Holocene to historical eruptions (witnessed and recorded since 1830; Scott, 2013) have all been sourced from vents that are currently submerged beneath the warm, acidic Crater Lake. Instabilities in the hydrothermal system lead to semi-regular heating cycles and irregular hydrothermal eruptions (Hurst et al., 1991; Vandemeulebrouck et al., 2005). Eruptions driven by magma ascent usually result in initial phreatic-phreatomagmatic activity (e.g., Reed, 1945; Houghton et al., 1987; Nairn et al., 1979; Johnston et al., 2000) followed by rare magmatic phases if the vent area is free of lake water (e.g., Houghton et al., 1987; Christenson, 2000; Johnston et al., 2000). Large volumes of Crater Lake water are often ejected onto the surrounding snow- and ice-covered slopes during phreatic

and phreatomagmatic eruptions, resulting in lahars down the glaciated valleys that surround the summit plateau (e.g., Cronin et al., 1997; Carrivick et al., 2009; Kilgour et al., 2010).

65 The eruptive history of Ruapehu has been compiled using written records and eyewitness accounts since 1830. Our compilation includes small-scale events such as phreatic/hydrothermal eruptions to the more significant phreatomagmatic/magmatic eruptions. From this dataset, it is apparent that phreatic eruptions occur much more frequently than phreatomagmatic eruptions, an important consideration when considering the frequency-magnitude relationship for hazard  
70 analysis (Fig 2).

A number of studies have examined the petrogenesis of Ruapehu magmas and all have concluded that an open magmatic system, involving small-volume distinct magma batches exists beneath the active vents (e.g., Gamble et al., 1999, 2003; Price et al., 2012; Kilgour et al., 2013). The mineralogy of Ruapehu andesite is consistent through time, with macrocrysts (including cog-  
75 nate crystals and antecrysts) of plagioclase, clinopyroxene, orthopyroxene and rare Fe-Ti oxides (in decreasing abundance). This mineral assemblage is consistent with a relatively dry magma composition ( $< 2\text{-}3 \text{ H}_2\text{O wt } \%$ ), lacking hydrous mineral phases (Price et al., 2012; Kilgour et al., 2013). There is no clear trend in the mineral content or abundance of Ruapehu magmas through time (Gamble et al., 1999; Kilgour et al., 2013) nor is there a clear crystallisation sequence (Price  
80 et al., 2012). Based on the analysis of melt inclusions within plagioclase and pyroxenes crystals, most historical eruptions contain macrocrysts that are foreign to the host (Kilgour et al., 2013), a common occurrence throughout the pre-historical lavas at Ruapehu (Price et al., 2012). Variable trapping pressures (from 0.5 to 3.0 kb) calculated from melt inclusion volatile contents, suggest that a complex of sills, dykes, and crystal mush zones exists from  $\sim 2$  to  $> 9$  km depth (Kilgour  
85 et al., 2013).

#### 4. Methods

Scoria samples available for this study were collected soon after eruptions in 1969, 1971, 1977, 1995 and 1996 (a lava sample from 1945 was excluded from the analyses here). Further details on the samples are described elsewhere (Kilgour et al., 2013). For each scoria sample, we lightly  
90 crushed, separated and mounted pyroxene and plagioclase crystals. Samples were then polished and carbon coated. Pyroxene and plagioclase crystals were examined with back-scattered electron (BSE) imaging using a Hitachi S-3500N SEM at the University of Bristol enabling the crystal zoning to be categorised. Where distinct zones were noted (by the greyscale variation in the BSE image), we then analysed a selection of these by Electron Probe Microanalyser (EPMA) to

95 quantify the greyscale variation in terms of major element composition, using beam conditions of 15 kV accelerating voltage, and a 10 nA focused beam. While both plagioclase and pyroxene crystals exhibited zoning, this study focusses solely on pyroxene. The variation in greyscale from a clinopyroxene (and orthopyroxene) BSE image is strongly correlated to its Fe-Mg content (e.g., Saunders et al., 2012b; Allan et al., 2013). The pixel diameter of our BSE greyscale images  
 100 is  $\sim 250 - 300$  nm. For comparison, a focused EPMA beam has an excitation volume of  $\sim 2$   $\mu\text{m}$ . Similar to Saunders et al. (2012a), many of the outermost rims examined are  $< 4$   $\mu\text{m}$ , so EPMA cannot sufficiently resolve the complexity within the zoning profile. However, EPMA does provide quantitative analyses along the profile that allow us to develop a transfer function between BSE greyscale intensity and composition.

105 We took a selection of pyroxene crystals (including microlites) that had been imaged by BSE and conducted semi-quantitative line scans and quantitative spot analyses, using a JEOL 8530F Field Emission Gun (FEG) EPMA at the University of Bristol. Beam conditions for the FEG EPMA were run at 5 and 9 kV, at 10 nA and with a focussed beam. We ran lines at two different voltages in order to minimise the excitation volume. At 5 kV, we analysed for Si, Mg, Ca and  
 110 Al, while at 9 kV, we measured for Fe, Si and Mg. FEG probe analyses are ideal for obtaining high spatial resolution where the distance between points can be reduced to  $\sim 300$  nm, using a  $\sim 30$  nm diameter spot (c.f. Saunders et al., 2014). Quantitative FEG analyses (discrete spots) along the line profile allowed us to quantify the line scan.

We followed the method of Morgan et al. (2004) when converting the BSE greyscale image,  
 115 FEG probe, and EPMA profiles. The primary assumption is that the initial profile between two zones follows a step function thus the maximum timescales are calculated. As diffusion commences, an initially steep profile will become progressively broader with time, commensurate with the element diffusion rate. BSE images were obtained from  $> 100$  pyroxene crystals that exhibited an outermost rim from five eruptions. This reduced the potential for bias towards any  
 120 one type of zoning pattern.

For our diffusion modelling, only congruent (regular and even) crystal boundaries were selected, with at least four analytical points on the slope between the two end member compositions (Costa and Morgan, 2010). To reduce the potential for anomalously stretched profiles, greyscale sections were analysed perpendicular to the crystal zone. Sectioning of a sample is invariably  
 125 not planar and so the zoning of a crystal can often be asymmetric. We took profiles across the narrowest zone in all cases and therefore our timescales are considered maxima (e.g., Saunders et al., 2014; Costa and Morgan, 2010). Where possible, we took more than one profile per crystal

and calculated the average. To quantify the greyscale profile, we obtained greyscale intensity values using the free software package ImageJ.

130 There are a number of factors that must be considered when converting the zoning pattern of a pyroxene crystal into a timescale. 1) We assume that crystal growth occurred rapidly and therefore the diffusion profile is solely related to chemical relaxation. 2) The diffusion rates of many elements have not been rigorously determined experimentally. We have used the best available diffusivities of Fe-Mg in clinopyroxene (Dimanov and Wiedenbeck, 2006; Müller et al., 135 2013) (which are very similar) and in orthopyroxene (Schwandt et al., 1998). Furthermore, the rate of diffusion may be different along varying crystal axes, however for clinopyroxene, this has yet to be determined experimentally and for orthopyroxene, there does not appear to be a significant difference (Schwandt et al., 1998; Cherniak and Dimanov, 2010). 3) Diffusion rates are known to be extremely sensitive to temperature (Cherniak and Dimanov, 2010). Consequently 140 an accurate estimate of the magmatic temperature is essential because small temperature variations will have a large effect on the final timescale. Kilgour et al. (2013) calculated magmatic temperatures from mineral-melt equilibria and Fe-Ti oxide geothermometry for selected historical eruptions to be 915 °C (1969), 958 °C (1971), 977 °C (1977), and 1030 °C (1995 & 1996). These eruption temperatures were mainly derived from orthopyroxene- and clinopyroxene-melt 145 geothermometers. As such, these temperatures are used for the diffusion modelling throughout. 4) We also assume that diffusion ceases on eruption, due to rapid cooling. 5) The oxidation state of the magma will affect the ability for  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  substitution in clinopyroxene, which also has a moderate effect on diffusivities. Kilgour et al. (2013) calculated an oxygen fugacity ( $f\text{O}_2$ ) at  $\sim$  the Nickel-Nickel oxide (NNO) buffer, based on coexisting magnetite and ilmenite. 150 This is in agreement with pre-historic Ruapehu magmas from Price et al. (2012). The diffusion coefficients for clinopyroxene (Dimanov and Wiedenbeck, 2006) and orthopyroxene (Schwandt et al., 1998) used in this study are given in Table. 1.

To illustrate the errors involved, we examined a clinopyroxene crystal from the 1971 eruption (1971gl.08b) with an outermost rim diffusion timescale of 86 days. With a magmatic temperature 155 of 958 °C and at an oxygen fugacity of NNO, a temperature variation of  $\pm 20$  °C propagates through to  $\sim 54$  (978 °C) and 139 (938 °C) days. When we consider variations in oxygen fugacity using the diffusivities from Dimanov and Wiedenbeck (2006), which Müller et al. (2013) show has little effect on clinopyroxene diffusivities, for the same crystal and a constant temperature (958 °C), a  $\Delta\text{NNO}$  of  $\pm 1$  log unit results in  $\sim 52$  (NNO+1) and 143 (NNO-1) days. Therefore, the 160 uncertainties in diffusion chronometry are significant, but are reasonable when determining the

broad timing of magmatic processes. We suggest that both the  $f\text{O}_2$  and temperature of Ruapehu magmas is reasonably well constrained, providing some confidence in the final timescale.

## 5. Results

### 5.1. pre-1995 Monitoring Data

Monitoring data from Ruapehu have been presented elsewhere including a compilation (1971-1996) of chemical and seismic data (Sherburn et al., 1999) and more recently the fluid and gas chemistry (2003-2008; Christenson, 2000), so only the key points are briefly summarised here. Seismicity at Ruapehu has not been a strong indicator of impending eruptions (Sherburn et al., 1999), as seen in volcano-tectonic earthquakes, which are common at Ruapehu. In general, earthquakes are generated at two depth intervals, a shallow component ( $< 1$  km beneath Crater Lake) within the hydrothermal system (Hurst, 1998), and a deeper zone within a probable dyke-sill complex (between  $\sim 2$  and  $> 9$  km; Kilgour et al., 2013). There are currently no indicators of eruption from the number and/or type of earthquakes. Based on these interpretations, eruptions were often considered to have occurred with little or no precursory activity. Before the 1995 eruption, only two or three short-period seismometers (four from 1993) were installed near the volcano (no seismometers to the west or south of the summit) and this may explain the lack of any meaningful precursory signal from 1969 to 1996 (Sherburn et al., 1999).

Crater Lake has been monitored since the 1960's for its fluid chemistry and lake temperature (Giggenbach and Glover, 1975). This temporal dataset allows us to assess precursory signals prior to magmatic eruptions (Fig. 3). A sensitive recorder of changes within the hydrothermal system (driven in part by the magmatic system), Crater Lake responds to temperature fluctuations from heat transferred within fluid and vapour (Hurst et al., 1991) and the composition of hydrothermal fluids, particularly when magma is injected into the hydrothermal system (Giggenbach and Glover, 1975). As a result, shallow magma degassing causes an increase in Cl within Crater Lake. An elevated Mg content of lake water is thought to be caused by hydrothermal alteration of shallow, fresh magma (Giggenbach and Glover, 1975). Such trends were observed immediately after the 1971 eruption and during the early stages of the 1995-1996 eruption episode (Christenson, 2000). This suggests that the Mg and Cl content of Crater Lake can be used to confirm the presence of magma within the hydrothermal system either before or after an eruption. Episodes of increased Mg and Cl content, and rising lake temperatures were measured on at least 5 occasions, 4 of which occurred immediately after a magmatic/phreatomagmatic eruption (1971, 1977, 1982 and 1995; Fig. 3).



### 5.2. Recent seismicity

More recently, an updated seismic network has recorded at least three periods of heightened  
195 seismicity, two of which occurred  $\sim 4$ -5 months before small-moderate phreatic eruptions on  
4 October, 2006 and 25 September, 2007 (Fig. 4). However, the seismicity preceding these  
eruptions were not considered to be precursors. With the aid of diffusion chronometry, we are  
now able to test whether these swarms could be used as a predictive tool in future, given similar  
timescales.

200 The seismic network at Ruapehu was upgraded in 2004 with the number of stations ap-  
proximately doubled. The upgraded network improved the detection and location capability of  
earthquakes on Ruapehu. The network has 16 stations within a 25 km radius of Mount Ruapehu  
and 8 stations on the volcano itself. We examined events within  $\sim 10$  km of Crater Lake. From  
2004 to 2013, 390 earthquakes were recorded that were comprised of 10 or more phases and were  
205 located without imposing a depth a priori. This ensured that we used only high quality locations.

Background rates of seismicity on Ruapehu are generally low, averaging a few events per  
month. From late March to early July, 2006, the number of earthquakes increased to a maximum  
of  $\sim 2$ -3 per day. Over a three month period, this resulted in 39 events. Rates of seismicity  
increased again from mid-January to mid-April, 2007 peaking at 10 events per day on 22 February,  
210 2007. Over this 3 month period, 74 events were recorded. The latest, albeit much smaller swarm,  
occurred between October and November 2012, peaking at 4 events per day with a total of 30  
events. Magnitudes of earthquakes detected were between 0.6 and 3.5M. The largest events  
occurred during the 2006 and 2007 swarms. During the 2006 swarm, most of the sequence was  
located between 12 and 18 km depth, while in 2007, earthquakes were mostly confined to between  
215 8 and 12 km. The 2012 swarm was sourced from a much shallower depth, generally between 1  
and 7 km. The differences in depths of the swarms is thought to be real as the depth variations  
are larger than the formal depth error estimates.

The location of seismicity around Ruapehu is predominantly west of Crater Lake with only a  
small number of events located on the east side. The 2006 swarm was located south of the cone,  
220  $\sim 7$ -10 km from Crater Lake, while the 2007 swarm was located WNW, at  $\sim 8$ -12 km from the  
vent. By contrast, the 2012 swarm was located within a 3 km radius of Crater Lake.

### 5.3. Petrological data

We examined 514 pyroxene (148 crystals in 1969; 58 in 1971; 102 in 1977; 96 in 1995; 110  
in 1996) macrocrysts ( $> 100 \mu\text{m}$ ) and more than 50 microlites ( $< 100 \mu\text{m}$ ) for this study.

225 Clinopyroxene and orthopyroxene are found in similar abundance in historical Ruapehu scoria  
 (Gamble et al., 1999; Kilgour et al., 2013). Clear compositional zoning is more common in  
 clinopyroxene than orthopyroxene. Typical Ruapehu clinopyroxenes are  $Wo_{\sim 42}$ ;  $En_{\sim 43}$ ;  $Fs_{\sim 15}$   
 (i.e. augite) and orthopyroxene are  $Wo_{\sim 3}$ ;  $En_{\sim 60}$ ;  $Fs_{\sim 27}$  (i.e. enstatite) (Kilgour et al., 2013).  
 Each crystal exhibits a dominant zoning pattern and we placed each crystal into general categories  
 230 of normal, reverse, multiple, patchy, and unzoned (Fig. 5). Crystals that exhibit normal zoning  
 have an Mg-rich core and Fe-rich rim, while a reverse zoned pyroxene has an Fe-rich core and  
 Mg-rich rim. Crystals that exhibit an alternating sequence of Mg-Fe-Mg or Fe-Mg-Fe from  
 core to rim (commonly observed in samples from 1995-1996) are classified as multiply zoned.  
 Crystals with patchy zoning have no clear core-rim profile. The population of each category  
 235 from a given eruption changes through time. For example, reversely zoned crystals in the 1995-  
 1996 eruptions are abundant, yet rare in 1969 (Fig. 5). These categories describe the dominant  
 zoning pattern, but on close inspection, many crystals exhibit a narrow ( $< 5-8 \mu m$  wide), dark  
 (Mg-rich) outermost rim (Fig. 6). Of the  $> 550$  crystals examined, 98 exhibited an Mg-rich  
 outermost rim, while only 6 had a Fe-rich rim. There was no clear difference in timescales  
 240 obtained from crystals of distinct zoning patterns, or between Mg- and Fe-rich rims. All suitable  
 crystals (macrocrysts and microlites) were analysed for diffusion timescales. All Mg-rich rims  
 have a similar width ( $\sim 3-8 \mu m$ ) except for pyroxene rims from 1996, which are consistently  
 wider (at  $\sim 5$  to  $20 \mu m$ ).

Greyscale profiles obtained from BSE images show that the outermost rim of all crystals  
 245 (macrocrysts and microlites) are relatively sharp. These rims appear as relatively dark grey  
 zones, which EPMA and FEG probe results confirm are due to Mg enrichment. The variation in  
 $SiO_2$  (with no coincident CaO content change) occurs over a narrower distance ( $\sim 0.9 \mu m$ ) than  
 the Mg or Fe ( $\sim 1.8 \mu m$ ) profiles. Using both the FEG line and greyscale intensity (similar spatial  
 resolution of  $\sim 300$  nm) profiles (Fig. 7), we used a simple 1-D diffusion model of Fe-Mg from  
 250 Morgan et al. (2004) with a diffusion coefficient dependant on oxygen fugacity and magmatic  
 temperature for both orthopyroxene and clinopyroxene (Fig. 8). Figure 8 shows that timescales  
 obtained from orthopyroxene are marginally shorter than those for clinopyroxene, which may  
 suggest that the diffusion coefficients are not yet fully comparable. Curves were fitted to the  
 observed diffusion profile, constrained by its upper and lower values and the slope between them.  
 255 FEG lines and greyscale profiles were in good agreement.

From both the FEG and SEM (greyscale) lines, and spot analyses, the dark, outer crystal  
 rims are of a different composition to the crystal core. The outermost rims of orthopyroxene

crystals are relatively enriched in MgO (by  $\sim 1$  wt %) compared to the lighter crystal cores, which are FeO-rich by  $\sim 1$  wt %. There appears to be no clear change in  $\text{Al}_2\text{O}_3$  or CaO across all orthopyroxene crystals (Fig. 7). Clinopyroxene crystal rims are enriched in MgO ( $\sim 1$  wt %) and CaO ( $\sim 0.5$  wt %) and depleted in FeO ( $\sim 1$  wt %). In backscattered SEM images, the outermost rim appears as a sharp boundary that follows the Fe-Mg compositional change (using FEG-EPMA line scans with a spacing of  $\sim 300$  nm). When compared to the  $\text{SiO}_2$  composition across this zone, we observe an increase over a larger distance (from  $\sim 1$  to  $2 \mu\text{m}$ ). It has been shown that the diffusivity of Si is significantly slower than Fe-Mg (Bejina and Jaoul, 1996; Sautter et al., 1988; Cherniak and Dimanov, 2010). The step change in  $\text{SiO}_2$  and CaO relative to the broad FeO-MgO profiles is evidence that the outer rim is composed of a distinct chemical composition to the crystal core.

Diffusion modelling gives the time between renewed crystal growth and eruption (Table 2; Fig. 9). Coupled with a known eruption date, the diffusion timescale provides a point in time at which the magma was perturbed. According to our data, a magmatic perturbation commenced  $\sim 5$ -7 months before each Ruapehu eruption, with the vast majority occurring within one to two months of the eruption. There is a weak trend in the data from the 1969 eruption because there were few crystals with an outer rim ( $n=13$ ). Conversely, for eruptions that exhibit common Mg-rich outermost rims, the data appear to be consistent and robust between eruptions. Importantly, each eruption tapped a magma of a different temperature (i.e., 1969 -  $915^\circ\text{C}$ ; 1971 -  $958^\circ\text{C}$ ; 1977 -  $977^\circ\text{C}$ ; 1995-1996 -  $1030^\circ\text{C}$ ) and hence were calculated using different diffusivities. Therefore, while the diffusivities varied, a similar modelled timescale exists between the different eruptions, using both clinopyroxene and orthopyroxene.

## 6. Discussion

In order to assess the timing of magmatic perturbations, we must first interpret and quantify the zoning profiles. Where present, crystal rims exhibit a sub-rounded interior indicative of resorption before eventual rim growth. To explore this further, we compared the compositions of Ruapehu pyroxenes with andesite experiments (Blatter and Carmichael, 1998; Moore and Carmichael, 1998) in an attempt to quantify the relative temperature and/or pressure changes needed to explain the change in pyroxene  $\text{Mg}_{\#}$  (molar % of  $\text{Mg}^{2+}$  to  $\text{Fe}^{2+}$ ). Blatter and Carmichael (1998) conducted their isobaric experiments at  $\sim 100$  MPa and at a range of temperatures, from  $950$  to  $1050^\circ\text{C}$ . Orthopyroxenes are relatively enriched in MgO i.e.,  $\text{Mg}_{\#88-91}$  with increasing magmatic temperature. The trend is less clear in clinopyroxene ( $\text{Mg}_{\#86,83,87}$

at 950, 1000, and 1050 °C respectively). Data from Moore and Carmichael (1998) are similar  
albeit with a more restricted dataset, whereby the Mg content of orthopyroxene increases with  
increasing temperature ( $Mg_{\#75-78}$ ). The composition of Ruapehu orthopyroxenes has a larger  
range ( $Mg_{\#52-72}$  for the crystal core vs  $Mg_{\#58-78}$  for the outermost rim). This may suggest  
that Ruapehu pyroxenes are derived from a range of pressure and temperature conditions to  
account for the spread in the compositions. Furthermore, the andesite experiments of Blatter  
and Carmichael (1998) and Moore and Carmichael (1998) were  $H_2O$  saturated while Ruapehu  
magmas are  $H_2O$  under-saturated (Kilgour et al., 2013), which could potentially account for  
the disparity between the natural and experimental crystal compositions. Nevertheless, the gen-  
eral trend in  $Mg_{\#}$  with temperature can be broadly used to show that resident mush zones or  
antecedent magmas were intruded by a fresh magma that was  $> 100$  °C hotter soon before erup-  
tion. This is similar to the interpretation put forward by Nakagawa et al. (1999, 2002) to explain  
the zoning patterns in Ruapehu pyroxenes from the 1995-1996 eruption episode. Therefore, the  
diffusion timescale that we measured must reflect the period of time after crystal resorption and  
rim growth caused predominantly by a rapid influx of high temperature magma, potentially with  
a distinct composition.

### 6.1. Implications of diffusion modelling

While we have shown that most Ruapehu pyroxene crystals record diffusion timescales  $< 7$   
months before eruption, the greatest proportion of magmatic interactions occurred on very short  
timescales ( $\sim 1-12$  weeks). If we assume that the Mg-rich crystal rims grew within a magma  
that had been heated by  $> 100$  °C, it is reasonable to suggest that a period of magma-magma  
or magma-crystal mush interaction led to the crystal rim growth. The dominant outermost rim  
is Mg-rich, while a small portion of pyroxenes exhibit a Fe-rich rim. Saunders et al. (2012a)  
suggested that gas fluxing could generate the Fe-rich rims, which appears a plausible explana-  
tion. Nakagawa et al. (1999, 2002) suggested that the interaction of magma and a crystal mush  
zone probably occurred during the 1995-1996 eruption sequence due to the presence of crystal  
cumulates, the variable magma compositions, the compositional variation across clinopyroxene  
rims, and the existence of a high and low temperature magma population. Kilgour et al. (2013)  
confirmed that magma-mush interactions occurred prior to most historical eruptions from the  
disparate composition and volatile content of melt inclusions and groundmass glasses. Based  
on these data, we interpret the very late-stage ( $\sim 1-12$  weeks) diffusion dates record the re-  
mobilisation of at least one crystal mush region before each eruption. This suggests that crystal

entrainment occurs rapidly in the rising magma and the rejuvenation of a crystal mush occurs in a matter of days to weeks.

At Ruapehu, interaction of distinct magma chambers within an open magmatic system occurs readily (Donoghue et al., 1995; Gamble et al., 1999) and as a result, it is unsurprising that foreign crystals could be entrained during the ascent of a relatively hot, gas-rich magma. The presence of crystal mush zones is further confirmed by the diffuse inner cores of many crystals, which if we assume a similar temperature to the final magmatic temperature (residence temperatures will be lower and consequently the diffusion would occur over significantly longer periods), crystals likely resided in the crust for periods in excess of 1000's years. The presence of multiply zoned crystals with an inner, Mg-rich band also suggests that periods of re-mobilisation without eruption also occurs. This implies that many crystals within a given scoria clast at Ruapehu are derived from long-lived crystal mush zones at depth.

## 6.2. Linking diffusion to pre-1996 monitoring data

The diffusion timescales calculated from outermost rims record magmatic perturbations before eruption, while the Crater Lake responds to changes in the hydrothermal system; in some cases caused by magma injection. When we compare the diffusion chronometry to the Crater Lake water chemistry, we note that there is no clear correlation. This implies that the processes occurring at depth within the dyke-sill complex were not able to liberate small volume magmas higher into the hydrothermal system until a short period before each eruption. This could be explained by the reduction in permeability in the hydrothermal system, restricting fluid flow into Crater Lake. Hurst et al. (1991) suggested that the presence of a liquid sulphur layer beneath the lake would control fluid and gas transfer depending on its temperature. At temperatures  $> 160$  °C, the viscosity of sulphur increases dramatically, resulting in a barrier to flow, while at temperatures  $> 200$  °C, the reduced viscosity would allow fluid and gas to flow (Hurst et al., 1991). Reduced permeability could also be caused by mineral precipitation, effectively sealing any free pore space.

Our more complete eruption history at Ruapehu records a large number of phreatic eruptions since 1830 (Fig. 2). Each phreatic eruption undoubtedly caused significant disruption to the hydrothermal system, resulting in open fractures that created pathways for fluid and gas flow. This allowed for the open exchange of fluid and gas from the hydrothermal system, yet we see no magmatic input into the lake prior to eruptions. Similarly, the seismic record from 1971 to 1996 shows no clear precursors (Bryan and Sherburn, 1999; Sherburn et al., 1999). During that

period, when the seismic network was limited, volcanic earthquakes occurred during eruptions,  
 355 but limited pre-event seismicity was observed. Therefore, injection of magma into the shallow  
 subsurface must have only occurred immediately before (days to weeks) all eruptions, in order  
 for the hydrothermal system to respond (Fig. 10). It is important to note here that the injection  
 of new magma into the mush zone will not always lead to an eruption. Indeed most magmatic  
 injections are unlikely to result in an eruption.

### 360 6.3. The 1995-1996 eruption sequence

From pyroxene crystals within 1995 scoria, magma mixing occurred in February-March, 1995  
 (Fig. 11). Crystal rims are of a similar width to previous eruptions, at  $\sim 3$  to  $8 \mu\text{m}$ . The increased  
 magma interactions leading up to the 1995 eruption point to late-stage re-mobilisation of one or  
 more crystal mush zones. This is in contrast to the June-July, 1996 eruptions. Timescales from  
 365 that eruption cluster around September-October, during the 1995 eruptions (Fig. 11). Crystal  
 rims from 1996 are significantly wider than those from 1996, at  $\sim 5$  to  $20 \mu\text{m}$ . Furthermore, a  
 small number of crystal rims from 1996 record mixing events before the phreatic eruptions in  
 February-March, 1995, similar to 1995 crystals. Such a close correlation with the 1995 samples  
 indicate that prior to the 1995 eruptions, a crystal mush zone (or zones) was intruded and  
 370 re-mobilised, entraining a small amount of foreign crystals into the ascending magma. The  
 stalled remnants of the 1995 magma were subsequently entrained into the 1996 magma (Kilgour  
 et al., 2013). That the rim width in 1996 scoria are significantly wider suggests a relatively long  
 residence, supporting this interpretation (Fig. 6).

The variation in pyroxene rim width from 1995 to 1996 affords us the opportunity to calculate  
 375 the growth rate of clinopyroxene and orthopyroxene, if we assume a constant growth rate. Given  
 that the average rim width in 1995 and 1996 is 6 and  $15 \mu\text{m}$  respectively (Fig. 6), and the  
 interval between these eruptions was  $\sim 8$  months, the growth rate is  $\sim 0.03 \mu\text{m}/\text{day}$  or  $\sim 10^{-10}$   
 cm/s. This growth rate is in good agreement with that calculated by Nakagawa et al. (2002),  
 who calculated growth rates from the  $\sim 6$  months of precursory phreatic activity prior to the  
 380 September, 1995 eruption.

### 6.4. Monitoring record since 2004

Seismicity and gas loss is generated during the pressurisation of a magma storage region, or  
 during magma ascent. Therefore, when compared to water chemistry, volcano seismicity and  
 airborne gas measurements are more likely to be more useful in predicting a future eruption at

385 Ruapehu. We will now explore the airborne chemistry and modern seismic signals at Ruapehu further.

Since regular gas monitoring was initiated in 2004, only three phreatic eruptions have occurred at Ruapehu (2006, 2007, and 2009) (Fig. 12). These events were small compared to historical phreatomagmatic eruptions, and of those eruptions, it has been proposed that the 390 2007 eruption was driven by magmatic gases (Christenson et al., 2010). Airborne CO<sub>2</sub> and SO<sub>2</sub> flux measurements, Crater Lake temperature, and lake composition remained at background levels (or gradually decreasing) immediately before each eruption (Christenson et al., 2010) (Fig. 13). During magma ascent and degassing, it is reasonable to expect an increase in lake temperature, Mg and Cl contents, and increased CO<sub>2</sub> and SO<sub>2</sub> fluxes within an open hydrothermal 395 system. Depending on the ascent rate, we would expect to see magmatic signatures weeks to months before an eruption. Instead, leading up to those phreatic eruptions, the lake temperature was decreasing while the Mg and Cl content of the lake remained static. This suggests that a permeability barrier existed, preventing gas and fluid from passing through the hydrothermal system and into Crater Lake. Immediately after the eruption, airborne gas measurements showed 400 a significant increase in CO<sub>2</sub> and SO<sub>2</sub> flux, indicative of magma injection into the hydrothermal system (Christenson et al., 2010).

The only monitoring method that appears to record magmatic processes on a similar timescale to diffusion chronometry is deep seismicity (Fig. 4). Prior to both the 2006 and 2007 phreatic eruptions, swarms of deep seismicity were recorded between 8 and 18 km depth. The trapping 405 pressures calculated from the H<sub>2</sub>O and CO<sub>2</sub> content of phenocryst-hosted melt inclusions, along with magnetotelluric (MT) soundings (Ingham et al., 2009) and seismic tomography (Rowlands et al., 2005) analysis all suggest that the magma storage region at Ruapehu resides between 2 and > 9 km depth. Therefore, it is entirely plausible that deep seismicity was a consequence of the injection of new magma into the base of the magma storage region. At ~ 5 to 7 months 410 before those phreatic eruptions, magma recharge may have initiated the pressurisation of the magma, thus resulting in concomitant diffusion timescales. This pressurisation period is similar to that observed at Mt. St. Helens (Saunders et al., 2012a).

## 7. Conclusions

We have compared diffusion timescales from five historical eruptions against a multi-parametric 415 monitoring dataset since mid-1960. Diffusion chronometry data show that the Ruapehu magmatic system was perturbed up to 7 months before most eruptions. The increased number of

diffusion dates towards the eruption suggests that magmatic interactions, especially involving crystal mush zones, occurred a matter of weeks before eruption. This is highlighted by the 1995 eruption, which erupted crystals that have a 3-8  $\mu\text{m}$  wide outer rim with a diffusion timescale of  
420 < 6 months before eruption. In contrast, crystals from 1996 exhibit a significantly wider outer rim ( $\sim 5\text{-}20\ \mu\text{m}$ ) and consequently record the same magma-mush event as the 1995 eruption. A short time before the 1996 eruption, new magma ascended and entrained the un-erupted portions of the 1995 magma, similar to the interpretation from melt inclusions (Kilgour et al., 2013) and previous work on the 1995-1996 eruption (Nakagawa et al., 1999, 2002).

425 We compared our diffusion timescales to Crater Lake fluid chemistry and temperature, yet we find that the Crater Lake exhibited significant changes immediately after a magmatic eruption and not before. Therefore, the hydrothermal system at Ruapehu does not react readily to magmatic intrusions, unless magma reaches very shallow levels and stalls. Instead, the reduction in pore space due to hydrothermal mineral growth and a liquid sulphur seal likely formed an  
430 effective barrier to the flow of fluids and gases into Crater Lake.

With an upgraded monitoring system since 2004, we find a potential link between our diffusion chronometry and deep seismicity before two phreatic eruptions in 2006 and 2007. Approximately 5 to 7 months before those eruptions, we observed a deep ( $\sim 8$  to 18 km) seismic swarm. We speculate that the seismicity recorded a magma recharge event that eventually led to the pres-  
435 surisation of a magma body, resulting in eruption. The increased  $\text{CO}_2$  and  $\text{SO}_2$  release after the 2007 event testifies to the likely involvement of magma in that eruption (Christenson et al., 2010).

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## 10. Table and Figure Captions

**Table 1.** List of diffusivities of Fe-Mg exchange for clinopyroxene (Dimanov and Wiedenbeck, 2006) and orthopyroxene (Schwandt et al., 1998). The oxygen fugacity ( $f_{O_2}$ ) is constant at the Nickel-Nickel oxide (NNO) buffer.

**Table 2.** Calculated diffusion timescales from 1-D modelling of Ruapehu pyroxenes.

**Figure 1.** (a) Located at the southern end of the Taupo Volcanic Zone (TVZ), Mt. Ruapehu is a frequently active andesitic, cone volcano. Samples available for this study were collected after each magmatic eruption. (b) The largest eruption ( $\sim 0.001 \text{ km}^3$ ) in the last 50 years was in 1995-1996. Scoria samples from all historical eruptions were ejected onto snow and ice on the upper slopes and cooled rapidly, which ensures that the diffusion profile is preserved. (c) An image from the 2007 phreatic eruption, which was driven by magmatic gases (Christenson et al., 2010). Phreatic eruptions are common at Ruapehu (see Fig. 2) but are difficult to predict.

**Figure 2.** Newly compiled history of Ruapehu eruptions (Scott, 2013). Records extend to 1830 and were drawn from newspaper and other eye-witness accounts. Most eruptions in historical times were phreatic, with only minor magmatic or phreatomagmatic events. The eruption scale is a subjective measure of the size and impact of each eruption. For example, an eruption of level 5 is large enough (sub-Plinian) to have a regional impact, while those of level 1-3 are confined to the lake basin and summit plateau. There is no record of any samples from historic eruptions before 1945.

**Figure 3.** Crater Lake temperature and fluid composition from 1966 to 2013, showing the elevated Mg and Cl concentrations immediately after magmatic eruptions (dashed, vertical red lines). Data courtesy of B. Christenson *pers. comm.*

**Figure 4.** Seismic data from 2004 to 2012 showing the seismic swarms that occurred  $\sim 5$ -7 months before two phreatic eruptions (vertical dashed lines) in 2006 (Mordret et al., 2010) and 2007 (Kilgour et al., 2013; Jolly et al., 2010; Christenson et al., 2010). Colour-coded for each earthquake swarm, the 2006 (light blue) and 2007 (dark blue) pre-eruption seismicity is located to the south and west of the vent respectively, similar to the distribution of seismicity before

the 1995 eruption (Sherburn et al., 1999). In contrast, the source of the 2012 (purple) swarm is located under the cone and at a depth of  $\sim 1\text{--}7$  km. Seismometer site locations are shown as triangles in the upper panel.

**Figure 5.** Crystal zoning patterns for historical Ruapehu scoria. Backscattered electron images of typical crystals that fall within each category are shown for comparison. Crystals preserve a history of magmatic interactions over a wide range of timescales. Where present, dark, outer rims exhibit relatively sharp diffusion boundaries and therefore record rapid changes in magmatic conditions soon before eruption.

**Figure 6.** Variations in the width of Mg-rich pyroxene crystal rims from Ruapehu. 1969, 1971 and 1977 pyroxenes exhibit a unimodal distribution and a narrow Mg-rich rims ( $\sim 3$  to  $8\text{ }\mu\text{m}$ ), while pyroxenes from the 1995 and 1996 eruptions are bimodal, with two modes at  $\sim 5$  and  $10\text{ }\mu\text{m}$ . Rims shown here are mostly Mg-rich (Mg), but rare Fe-rich (Fe) rims are also present. The increased rim width of 1996 pyroxenes (relative to 1995) is due to extended residence since the 1995 eruption.

**Figure 7.** a) An example pyroxene microlite and b) its compositional profile (from core to rim) across a typical Mg-rich rim. This crystal is from 1971 (1971\_gl07a2) and its composition was derived using the FEG-EPMA. The 9 kV line scan has a  $\sim 300\text{ nm}$  spacing. The diffusivities of Mg and Fe are faster than Si, therefore the Mg and Fe curves are broader ( $\sim 1.8\text{ }\mu\text{m}$ ) compared to Si ( $\sim 0.9\text{ }\mu\text{m}$ ). There is no variation in CaO content across the inner-rim boundary. These semi-quantitative FEG lines (based on counts) are calibrated by quantitative spot analyses. The diffusion timescale recorded by this zone is  $\sim 27$  days. Scale bar in the BSE image is  $10\text{ }\mu\text{m}$ .

**Figure 8.** A comparison of diffusion timescales between orthopyroxene and clinopyroxene crystals. Note that all of these timescales are from Mg-rich outermost rims as there were no Fe-rich rims observed in pyroxenes within 1971 scoria. This plot includes both macrocrysts and microlites (crystal  $<100\text{ }\mu\text{m}$  across) from the 1971 eruption, but similar agreement is seen in other eruptions. The diffusion coefficient used for orthopyroxene is from Schwandt et al. (1998) at a magmatic temperature of  $958\text{ }^{\circ}\text{C}$  (Kilgour et al., 2013). For clinopyroxene, we used the diffusion coefficient of Dimanov and Wiedenbeck (2006) with an oxygen fugacity fixed at NNO (Price et al., 2012; Kilgour et al., 2013). Filled diamonds represent timescales calculated at  $958$



°C, while the range of values extends from 978 to 938 °C.

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**Figure 9.** Diffusion dates calculated for each eruption. Timescales have been binned by month before the known eruption date. Perturbations to the magmatic system occurred at a similar time ( $\sim 7$  months) before all eruptions. A small number of crystals record the initial injection into the source magma, with an ever-increasing number of crystals recording late-stage magmatic injections soon before each eruption. Perturbations to the magmatic system increasingly occur before the eruption. In most cases, an injection of new magma disturbed the magmatic system within a month of the eruption. This implies that magma interaction occurred slowly and then rapidly increased before eruption. These dates were determined from macro-crysts (up to 2 mm) and microlites ( $< 100 \mu\text{m}$ ). Eruptions are shown by the dotted black lines.

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**Figure 10.** Compilation of diffusion timescales, and monitoring data from 1960 to 1996. Eruption history has been compiled from written accounts. Crater Lake water samples were sampled monthly and analysed for Cl and Mg; two elements indicative of magmatic injection into the hydrothermal system Giggenbach and Glover (1975). In most cases, elevated Cl and Mg contents were recorded after a magmatic eruption. Seismic data is limited due to the sparse seismic network during this period. Eruptions are delineated by dashed black lines. Diffusion data (lower panel) are plotted with the same colours as Fig (9)

**Figure 11.** Time-series plot of monitoring data and diffusion dates for the 1995-1996 eruption. Crater Lake chemistry records magmatic input during and immediately after eruptions. Increases in Cl content is related to fumarolic degassing at shallow depths while an increase in Mg is caused by hydrothermal alteration of the fresh magma (Giggenbach, 1974). Prior to the 1995 eruption, frequent, small phreatic eruptions maintained a highly permeable hydrothermal system. This allowed for magmatic fluids to be transported into Crater Lake, probably caused by shallow-seated magma.

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**Figure 12.** Airborne gas chemistry measurements at Ruapehu from 2004 to 2013. Some of these data (2004 to 2010) has been presented elsewhere (Christenson et al., 2010). Note the elevated  $\text{CO}_2$  and  $\text{SO}_2$  flux soon after the 2007 eruption.

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**Figure 13.** Crater Lake fluid composition from 2004 to 2013, showing the limited change

observed either before or after recent phreatic eruptions (dashed, vertical blue lines). A slight increase in Mg soon after the 2007 eruption signals the shallow degassing of fresh magma (Christenson et al., 2010).

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## 11. Figures and Tables

Table 1

Temperature (°C)	Clinopyroxene (m <sup>2</sup> /s)	Orthopyroxene (m <sup>2</sup> /s)
915	1.67023 x 10 <sup>-21</sup>	9.68508 x 10 <sup>-21</sup>
958	3.39797 x 10 <sup>-21</sup>	2.47228 x 10 <sup>-20</sup>
977	4.55055 x 10 <sup>-21</sup>	3.66448 x 10 <sup>-20</sup>
1030	9.74581 x 10 <sup>-21</sup>	1.03378 x 10 <sup>-19</sup>

Table 2

1969			1971			1977			1995			1996		
Sample number	Days	Sample number	Days	Sample number	Days	Sample number	Days	Sample number	Days	Sample number	Days	Sample number	Days	Sample number
1969_08A	593	1971Agl_7	122	1977_01a	509	1995A_01A	198	1996-01	298					
1969_12a	302	1971Agl_8	147	1977_03b	23	1995A_022	105	1996-02	272					
1969_24b	188	1971A_09A	457	1977A_03A	45	1995A_023	34	1996-06	297					
1969_49a	84	1971A_05a	38	1977A_10A	197	1995A_03A	21	1996-04	28					
1969_47a	72	1971A_06a	65	1977A_12A	96	1995A_04	195	1996-02a	178					
1969_46a	161	1971A_07a	102	1977A_20A	9	1995A_05	356	1996-17a	475					
1969_44a	112	1971A_09a	68	1977A_21A	19	1995A_06a	329	1996-18a	280					
1969_43a	37	1971gl_01a1	96	1977A_22A	13	1995B_05	51	1996-22a	70					
1969_41a	14	1971gl_01a2	123	1977A_23A	11	1995B_04a	81	1996-24a	393					
1969_34a	18	1971gl_01b	54	1977A_24A	19	1995B_13a	197							
1969_12a	194	1971gl_02a	25	1977A_25A	9	1995B_20a	21							
		1971gl_03a	20	1977A_26A	16	1995B_21a	47							
		1971gl_04a	39	1977A_28A	444	1995B_22a	37							
		1971gl_05a	205			1995B_23a	21							
		1971gl_06a	27			1995B_24a	4							
		1971gl_06b	67			1995B_25a	252							
		1971gl_07a	23			1995B_26a	335							
		1971gl_07b	318			1995B_27a	11							
		1971gl_08a	22			1995B_29a	64							
		1971gl_08b	86											
		1971gl_09a	33											

Table 2

1969		1971		1977		1995		1996	
Sample number	Days	Sample number	Days	Sample number	Days	Sample number	Days	Sample number	Days
		1971gl_09b	17						
		1971gl_10a	12						

Days refers to diffusion timescales in days before eruption

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13